I.

The Detection of Mannite in Alkaline Solutions of Copper Sulphate

Combustion of Mannite by Alkaline Solutions of Potassium Permanganate in the Presence of Copper Sulphate

II.

A Determination of the Volumes of Weight ---Normal Solutions of Cane Sugar at 15°, 20°, 25°, and 30°

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY
HENRY OTTO EYSSELL,
BALTIMORE,
1912.

GEO. W. KING PRINTING CO.,
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ACKNOWLEDGMENT.

The author wishes to express his sincere gratitude to President Remsen, Professors Morse, Jones, Acree, Lovelace and Whitehead for instruction received in the lecture room and in the laboratory.

To Professor Morse, the writer wishes to express especial thanks for his personal direction of these investigations and also to Drs. Frazer and Holland for many valuable suggestions.

PART 1.

The Detection of Mannite in Alkaline Solutions of Copper Sulphate.

The measurement of the osmotic pressure of solutions, which has been in progress in this laboratory for the last ten or twelve years, for the purpose of determining whether this force obeys the laws of gas pressure or not, has thus far been confined mainly to solutions of cane sugar and glucose. As soon as practicable, other substances will be dealt with, and mannite will probably be one of the first of these.

In the work with cane sugar and glucose, changes in the concentration of their solutions can be detected by means of the polarimeter. This method can not be employed in the case of mannite, which made it desirable to work out another for this substance just as delicate, or even more so, than the one based upon the rotatory power of cane sugar and glucose.

When the cells containing the solutions whose osmotic pressure is to be measured, are set up, they are immersed in a vessel containing an 0.01th ion N, solution of copper sulphate, while the cells themselves always contain a quantity of an 0.01 ion N. solution of potassium ferrocyanide besides the solutions in question. These quantities are believed to be osmotically equivalent, and they are used in this manner for the purpose of repairing ruptures which may develop in the membrane while the cells are giving a measurement.

It was found that when a solution of mannite is made alkaline with potassium hydroxide and there is then added to it a small quantity of copper sulphate, *a fine blue color is developed without precipitation of copper hydroxide. If more copper sulphate is added, a precipitate of copper hydroxide appears, and if still more of the copper sulphate is added, the fine blue*

color referred to eventually disappears, leaving the mannite uncombined with the copper, but still in solution.

At temperatures between 0° and 60°, all solutions are made up with 0.001 N. thymol water to prevent the growth of the mould penicillium glaucum, which it seems, thrives upon the nitrogen of the ferrocyanogen anion of the membranes and destroys them. It was possible that the thymol might affect this color reaction, or give a similar one under the same conditions, but such was found not to be the case. When solutions of copper sulphate containing thymol in quantities sufficient to make them 0.001 N. with respect to the latter substance, are treated with a solution of potassium hydroxide and filtered through asbestos the filtrates are clear and colorless.

This, then, seemed to be a practicable method for detecting the presence of mannite in solution when other substances which act similarly are known to be absent. Several other poly-acid alcohols (glycerol, erythrite and arabite) were found to conduct themselves in an analogous manner.

The solutions of copper sulphate and of mannite used in the subsequent work, were made up with .001 N. thymol water, while the solution of potassium hydroxide was made up with pure water. The solutions of copper sulphate were 0.1 and 0.01 volume normal, that of potassium hydroxide was approximately 0.5 N., each cubic centimeter containing .02805 grams. The solution of mannite contained one milligram of the alcohol per cubic centimeter.

Table 1 contains the quantities of mannite and the maximum quantities of copper sulphate, which in 100 cubic centimeters of solution, were found to give a blue colored filtrate after the addition of 5 cubic centimeters of the potassium hydroxide solution. When the copper sulphate exceeded the quantities tabulated by one-tenth of a milligram, the filtrates became practically colorless.

TABLE 1.

Mannite.	Maximum Quantities of Copper Sulphate.
1 mg.	37 mg.
2 mg.	88 mg.
3 mg.	107.8 mg.
4 mg.	144.0 mg.
5 mg.	180.0 mg.
6 mg.	187.1 mg.
7 mg.	198.3 mg.
8 mg.	236 mg.
9 mg.	245.4 mg.
10 mg.	261 mg.

Table 2 contains the results which were obtained when an attempts was made to duplicate those given in Table 1. The cause for whatever discrepancies there are between the results in the two tables was found to be due to the fact that the asbestos filter absorbs and retains some of the coloring matter.

TABLE 2.

Mannite.	Maximum Quantities of Copper Sulphate.
1 mg.	36.3 mg.
1 mg.	32.2 mg.
2 mg.	88.0 mg.
2 mg.	97.9 mg.
3 mg.	121.4 mg.
3 mg.	131.4 mg.
4 mg.	144.0 mg.
4 mg.	153.9 mg.
5 mg.	179 9. mg.
5 mg.	177.7 mg.
6 mg.	158.8 mg.

Table 3 contains the quantities of copper sulphate and the minimum quantities of mannite which, in 100 cubic centimeters of solution, were found to give a characteristically colored filtrate after adding 5 cc. of the alkali solution.

TABLE 3.

Copper Sulphate.	Minimum Quantity of Mannite.
10 mg.	0.3 mg.
20 mg.	0.5 mg.
30 mg.	0.6 mg.
40 mg.	1.1 mg.
50 mg.	1.4 mg.

Table 4 contains the quantities of mannite and the maximum quantities of copper sulphate, which were found to give the colored filtrate in 200 cc. of solution after adding 5 cc. of the alkali solution.

TABLE 4.

Mannite.	Maximum Quantity of Copper Sulphate.
1 mg.	34 mg.
2 mg.	64 mg.
3 mg.	92 mg.
4 mg.	122 mg.
5 mg.	154 mg.

Table 5 contains the quantities of copper sulphate and the minimum quantities of mannite, which were found to give a colored filtrate in 200 cc. of solution, after making alkaline with 5 cc. of the potassium hydroxide solution.

TABLE 5.

Copper Sulphate.	Minimum Quantity of Mannite.
10 mg.	0.4 mg.
20 mg.	0.7 mg.
30 mg.	0.9 mg.
40 mg.	1.3 mg.
50 mg.	1.6 mg.

Tables 6 and 7 contain the results obtained in 100 cc. of solution when the ratio of mannite to copper sulphate was kept constant. The mode of proceedure here and in the following cases was the same as stated above.

TABLE 6.

Mannite.	Copper Sulphate.	Filtrate.
1 mg.	25 mg.	Colored.
2 mg.	50 mg.	Colored.
3 mg.	75 mg.	Colored.
4 mg.	100 mg.	Colored.
5 mg	125 mg.	Colored.
6 mg.	150 mg.	Colored.
7 mg.	175 mg.	Colored.
8 mg.	200 mg.	Colored.
9 mg.	225 mg.	Colored.
10 mg.	250 mg.	Colorless.

The last filtrate was colored, when 10 instead of 5 cc. of alkali were used.

TABLE 7.

Mannite.	Copper Sulphate.	Filtrate.
1 mg.	30 mg.	Colored.
2 mg.	60 mg.	Colored.
3 mg.	90 mg.	Colored.
4 mg.	120 mg.	Colored.
5 mg.	150 mg.	Colored.
6 mg.	180 mg.	Colored.
7 mg.	210 mg.	Colored.
8 mg.	240 mg.	Colorless.
9 mg.	270 mg.	Colorless.
10 mg.	300 mg.	Colorless.

TABLE 8.

Mannite.	Copper. Sulphate.	Alkali.	Filtrate.
1 mg.	60 mg.	140.3 mg.	Colorless.
1 mg.	60 mg.	500.0 mg.	Colorless.
1 mg.	70 mg.	500.0 mg.	Colorless.
1 mg.	80 mg.	500.0 mg.	Colorless.
1 mg.	90 mg.	500.0 mg.	Colorless.

The filters were washed with 10 cc. of the alkali solution. The washings were all colored.

Asbestos filters were used throughout. A new batch of asbestos was prepared at this stage of the work. It was considerably finer than that previously used, and with it colorless filtrates were obtained with ratios which had given colored ones before, as may be seen from the results given in table 9.

TABLE 9.

Mannite.	Copper Sulphate.	Alkali.	Filtrate.
1 mg.	25 mg.	500 mg.	Colorless.
1 mg.	25 mg.	750 mg.	Colorless.
1 mg.	25 mg.	1000 mg.	Colorless.
1 mg.	25 mg.	1250 mg.	Colorless.

When the filters were washed with 10 cc. of the alkali the washings were not colored. They were deeply colored, however, when alkali of Fehling's solution strength was used. Blank experiments gave colored washings with the strong alkali, but not with 0.5 N.

TABLE 10.

The solutions were made alkaline with 5 cc. of the potassium hydroxide solution.

Mannite.	Copper Sulphate	Filtrate.
1 mg.	25 mg.	Colorless.
2 mg.	50 mg.	Colorless.
3 mg.	75 mg.	Colored.
4 mg.	100 mg.	Colored.
5 mg.	125 mg.	Colored.
6 mg.	150 mg.	Colored.

The filters were allowed to stand for about 15 minutes with 10 cc. of 0.5 N. alkali. The washings were all colored.

TABLE 11.

Mannite.	Copper Sulphate.	Filtrate.
1 mg.	50 mg.	Colored.
2 mg.	100 mg.	Colored.
3 mg.	150 mg.	Colorless.
4 mg.	200 mg.	Colorless.
5 mg.	250 mg.	Colorless.
6 mg.	300 mg.	Colorless.

The filters were allowed to stand for about 15 minutes with 10 cc. of the 0.5 N. alkali. The washings were all colored.

TABLE 12.

Mannite.	Copper Sulphate.	Filtrate.
1 mg.	75 mg.	Colorless.
2 mg.	150 mg.	Colorless.
3 mg.	225 mg.	Colorless.
4 mg.	300 mg.	Colorless.
5 mg.	375 mg.	Colorless.
6 mg.	450 mg.	Colored.
7 mg.	525 mg.	Colored.

The filters were allowed to stand with 0.5 N. alkali as stated. The washings were all colored, excepting those obtained from the 5 and 7 mg. experiments. Duplicate experiments gave the same results.

TABLE 13.

The solutions were made alkaline with 5 cc. of the potassium hydroxide solution.

Mannite.	Copper Sulphate.	Filtrate.
1 mg.	100 mg.	Colorless.
2 mg.	200 mg.	Colorless.
3 mg.	300 mg.	Colorless.
4 mg.	400 mg.	Colored.
5 mg.	500 mg.	Colored.
6 mg.	600 mg.	Colored.

The filters were treated with 0.5 N. alkali as stated. Where colorless filtrates were obtained the washings were colored, and vice versa.

TABLE 14.

The solutions were made alkaline with 5 cc. of the potassium hydroxide solution.

Mannite.	Copper Sulphate.	Filtrate.
1 mg.	10 mg.	Colored.
2 mg.	20 mg.	Colored.
3 mg.	30 mg.	Colored.
4 mg.	40 mg.	Colored.
5 mg.	50 mg.	Colored.
6 mg.	60 mg.	Colored.

The filters were treated as in previous cases; the washings were all colored.

The results tabulated in tables 6 to 14, inclusive, were obtained in 100 cc. of solution. Those given in table 15 were obtained in 100 cc. of .01 N. copper sulphate solution.

TABLE 15.

Mannite.	Copper Sulphate.	Alkali.	Filtrate.
1 mg.	123.92 mg.	5 cc. 140.3 mg.	Colorless.
1 mg.	123.92 mg.	10 cc. 280.5 mg.	Colorless.
1 mg.	123.92 mg.	15 cc. 420.8 mg.	Colorless.
1 mg.	123.92 mg.	20 cc. 561.0 mg.	Colorless.
1 mg.	123.92 mg.	25 cc. 701.3 mg	Colorless.
1 mg.	123.92 mg.	30 cc. 841.5 mg.	Colorless.
1 mg.	123.92 mg.	40 cc. 1122.0 mg.	Slightly Colored.
1 mg.	123.92 mg.	45 cc. 1162.5 mg.	Slightly Colored.
1 mg.	123.92 mg.	50 cc. 1402.5 mg.	Slightly Colored.
2 mg.	123.92 mg.	5 cc. 140.3 mg.	Colorless.
2 mg.	123.92 mg.	30 cc. 841.5 mg.	Colored.
2 mg.	123.92 mg.	50 cc. 1420.5 mg.	Colored.
3 mg.	123.92 mg.	30 cc. 841.5 mg.	Colored.
5 mg.	123.92 mg.	30 cc. 841.5 mg.	Deep Color.
None.	123.92 mg.	30 cc. 841.5 mg.	Colorless.
None.	123.92 mg.	50 cc. 1420.5 mg.	Colorless.

The color of the filtered solutions is probably due to the formation of one of the following compounds:

(1) $CH_2OH(CHOH)_4CH_2OH + 6Cu(OH)_2 \rightarrow CH_2OCuOH(CHOCuOH)_4CH_2OCuOH + 6H_2O$

(2) $2C_6H_8(OH)_5OH + Cu(OH)_2 \rightarrow C_6H_8(OH)_5O\,Cu\,O(OH)_5C_6H_8 + 2H_2O$

(3) $CH_2OH(CHOH)_4CH_2OH + 3Cu(OH)_2 \rightarrow \begin{matrix} CH_2O \\ | \\ CHO \end{matrix}\!\!\Big\}Cu + \begin{matrix} CHO \\ | \\ CHO \end{matrix}\!\!\Big\}Cu + 6H_2O + \begin{matrix} CHO \\ | \\ CH_2O \end{matrix}\!\!\Big\}Cu$

Working with molecular ratios in 100 cc. of solution, it was found that, at proportions lower than 1 of mannite to 3 of copper sulphate, no precipitate was formed, and the color of the solutions increased in intensity upon the addition of 5 cc. of 0.5 N. potassium hydroxide solution. The color of the solution in which mannite and copper sulphate were present in the proportion of 1 to 3.5, was no deeper than that of the 1 to 3 solution, and a slight precipitate could be detected in it. These facts would seem to indicate that the color in the case of mannite is due to the formation of compound No. 3.

Some experiments were made to determine whether nickel salts as well as those of copper could be employed for the detection of mannite, but with negative results.

Conclusions.

(1) The colored compound, whatever it may be, which is formed when a little copper sulphate is added to an alkaline solution of mannite, is decomposed by an excess (which is probably a definite one) of copper sulphate for every quantity of mannite. The alcohol is left in solution, but uncombined with copper.

(2) Although the colored compound is absorbed, more or less, by the asbestos of the filters, it can be removed from them by washing with alkali. In nearly every case where colorless filtrates were obtained while working with proportions, which had in previous experiments given colored ones, the alkaline washings from the filters were colored.

(3) Alkali of the strength used in Fehling's solution can not be employed for the washing of filters, because it dissolves copper hydroxide, giving a blue solution, while hot water has no effect whatever when used for washing purposes.

Although mannite cannot be determined quantitatively by the method described, it will serve very well for the detection of mannite in the liquid exterior to the osmotic cell when leakage through the membrane is suspected. By means of it two milligrammes can easily be detected in the presence of 123.92 milligrammes of copper sulphate in 100 cc. of liquid. Since the osmotic pressure of a 0.5 N. solution of mannite is about 12.5 atmospheres, a change of two milligrammes in its concentration would make a difference of .00028 of an atmosphere in the osmotic pressure developed.

Combustion of Mannite by Alkaline Solutions of Potassium Permanganate in the Presence of Copper Sulphate.

The next question to come under consideration in this connection, was that of finding some method for the quantitative determination of mannite, and its oxidation by means of potassium permanganate seemed an appropriate one.

Theoretically, thirteen atoms of oxygen are necessary for the complete combustion of every molecule of pure mannite.

This was verified, experimentally, as may be seen from the results given in the following tables:

TABLE 1.

Mannite.	KOH.	$KMnO_4$.	$CuSO_4$.	Temp. and Time in Bath.	$KMnO_4$, Reduced.	Atoms of Oxygen used.
1 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50°	4.3 mg.	12.38
1 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	4.4 mg.	12.67
1 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	4.8 mg.	13.82
1 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	4.5 mg.	12.96
1 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	4.4 mg.	12.67
None	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	None	None
2 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	9.2 mg.	13.24
2 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	9.1 mg.	13.10
2 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	9.0 mg.	12.96
2 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	8.8 mg.	12.67
2 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	9.1 mg.	13.10
None	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	None	None
3 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	13.31 mg.	12.78
3 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	13.18 mg.	12.64
3 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	13.18 mg.	12.64
3 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	13.62 mg.	13.07
3 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	13.18 mg.	12.64
None	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	None	None
4 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	17.85 mg.	12.84
4 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	18.16 mg.	13.07
4 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	17.78 mg.	12.81
4 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	17.72 mg.	12.67
4 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	20.09 mg.	14.47
None	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	None	None
5 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	22.70 mg.	13.10
5 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	22.51 mg.	12.96
5 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	22.55 mg.	13.10
5 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	22.76 mg.	13.10
5 mg.	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	22.70 mg.	13.10
None	5 cc.	93.27 mg.	123.92 mg.	19 hours at 50	None	None

TABLE 2.

Mannite.	KOH.	$KMnO_4$.	$CuSO_4$.	Temp. and Time in Bath.	$KMnO_4$. Reduced.	Atoms of Oxygen used.
10 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50°	45.70 mg.	13.15
10 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	45.45 mg.	13.09
10 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	45.20 mg.	13.02
10 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	45.33 mg.	13.05
10 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	45.39 mg.	13.07
None	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	None	None
20 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	90.28 mg.	12.99
20 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	90.53 mg.	13.04
20 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	90.07 mg.	12.96
20 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	90.07 mg.	12.96
20 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	90.22 mg.	12.99
None	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	None	None
30 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	135.1 mg.	12.97
30 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	135.2 mg.	12.99
30 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	135.1 mg.	12.97
30 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	135.05 mg.	12.97
30 mg.	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	135.1 mg.	12.97
None	5 cc.	187.05 mg.	123.92 mg.	19 hours at 50	None	None
40 mg.	10 cc.	361.01 mg.	123.92 mg.	19 hours at 50	180.95 mg.	13.02
40 mg.	10 cc.	361.01 mg.	123.92 mg.	19 hours at 50	181.59 mg.	13.08
40 mg.	10 cc.	361.01 mg.	123.92 mg.	19 hours at 50	182.24 mg.	13.11
40 mg.	10 cc.	361.01 mg.	123.92 mg.	19 hours at 50	181.21 mg.	13.05
40 mg.	10 cc.	361.01 mg.	123.92 mg.	19 hours at 50	181.46 mg.	13.08
None	10 cc.	361.01 mg.	123.92 mg.	19 hours at 50	None	None
50 mg.	10 cc.	432 mg.	123.92 mg.	19 hours at 50	224.56 mg.	12.93
50 mg.	10 cc.	432 mg.	123.92 mg.	19 hours at 50	224.09 mg.	12.90
50 mg.	10 cc.	432 mg.	123.92 mg.	19 hours at 50	224.56 mg.	12.93
50 mg.	10 cc.	432 mg.	123.92 mg.	19 hours at 50	223.58 mg.	12.89
50 mg.	10 cc.	432 mg.	123.92 mg.	19 hours at 50	223.96 mg.	12.90
None	10 cc.	432 mg.	123.92 mg.	19 hours at 50	None	None

The solutions used were made up with water containing no thymol.

It was found that the combustion is not complete until the reacting substances have been allowed to stand for a period of 19 hours at 50°. A quantity of potassium tetroxalate equivalent to the permanganate used was then added, and the excess of tetroxalate titrated back with the standard permanganate solution; the difference between the two quantities of permanganate added being the amount of permanganate reduced during the combustion.

The mannite used in this work was analyzed by the electrical method for the combustion of organic compounds, as devised by Professor Morse, and found to be practically pure.

Analysis No. 1—Mannite used, .0909 gms.
Per cent. hydrogen found, 7.96.
Per cent. hydrogen theoretical, 7.75.
Per cent. carbon theoretical, 39.54.
Per cent. carbon found, 39.47.
Per cent. purity, 100.2.

Atoms of oxygen necessary for complete combustion 13.03.

Analysis No. 2—Mannite used, .0918 gms.
Per cent. hydrogen found, 7.55.
Per cent. hydrogen theoretical, 7.75.
Per cent. carbon theoretical, 39.54.
Per cent. carbon found, 39.27.
Per cent. purity, 99.01.

Atoms of oxygen necessary for complete combustion 12.87

This method can be used for the quantitative determination of mannite in solutions of copper sulphate. The reducing action of thymol upon alkaline solutions of potassium permanganate is, however, considerably greater than that of mannite, which will probably necessitate the finding of some other means for coping with penicillium.

PART 2.

A Determination of the Volumes of Weight-Normal Solutions of Cane Sugar at 15°, 20°, 25° *and* 30°[1].

It is a well known fact that a contraction in volume takes place when sugar is dissolved in water at ordinary temperatures, that is, the volume of the solution is not the sum of the volumes of the water and sugar it contains. Determinations of the volumes of sugar solutions at 0°, made in this laboratory a few years ago, indicated that when a gram-molecular weight of sugar is dissolved in 1000 grams of water at that temperature, the volume of the solution is about 12 cc. less than the total volume of the water and sugar composing it.

This investigation was undertaken for the purpose of throwing some light on the amount of contraction occurring at 15°, 20°, 25° and 30° in solutions of cane sugar of the concentrations thus far used in the measurement of osmotic pressure, for it is hoped that a careful study of their behavior will be of value in explaining in a satisfactory manner the irregularities in the pressures developed by them at lower temperatures.

Figure 1 represents the apparatus used in making the measurements. It consists of a bulb having a capacity of about 100 cc., and a graduated stem of an inner diameter of about 4 mm. To this, at (c), is fused a calibrated tube about 400 mm. in length, having an interior diameter of about 2 mm. The exact volume of the apparatus up to the 0 mark on the graduated stem, was determined by weighing the bulb with water of a known temperature. In a similar manner the capacity of the stem between the 0 and 100 marks was also determined. The tube was calibrated between the scratches (a) and (b), and

1. This investigation was carried out in collaboration with Mr. F. S. Dengler, in whose dissertation the results obtained for the even concentrations may be found.

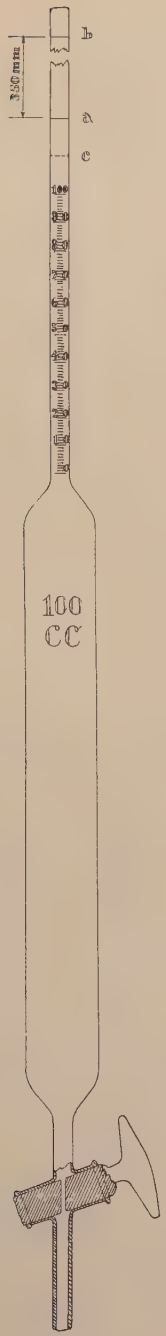

FIGURE 1.

after it had been fused onto the bulb, the volume of the space between the 100 mark on the stem and the lower scratch (a) of the tube was determined by means of a mercury thread.

Eleven such pieces of apparatus were prepared in the manner described, and weighed. Ten of the pieces were then filled with the sugar solutions and the remaining one with air-free water to some point a little above the lower scratch (a) on the calibrated tube.

A day or so after the apparatuses had been filled and placed in the constant temperature bath, all of them were found to leak around the stop-cocks to a greater or less extent. They were taken down, and after the stop-cocks had been carefully reground with very fine emory until they were tight, the apparatuses were filled again as before.

The first measurements were made at 15°, and in order to avoid the sticking of the liquid to the walls of the tubes, the solutions and water were cooled below this temperature before filling the dilatometers.

To secure reliable determinations of this nature, it is of the utmost importance that the apparatus be kept at a uniform temperature during the experiments, and that any slight changes in temperature which may occur shall be very gradual. In order to secure this uniformity of temperature, a constant temperature bath, originally devised by Morse and Frazer and described as at present employed in volume 44 of the American Chemical Journal, was used in these experiments.

A slight change was necessary in the construction of the bath. The galvanized iron cans used to hold the cells during the measurement of osmotic pressure were replaced by a copper trough large enough to contain all of the apparatuses at the same time. In a bath of this kind temperature fluctuations hardly exceed .01 of a degree.

After allowing the dilatometers to stand in the bath at the temperature in question for a period of twenty-four hours or more, the volumes of the solutions contained in them were read by means of a cathetometer. Readings were then taken from

day to day until the last three or four consecutive readings remained constant.

When the necessary readings had been made over the desired range of temperature, the apparatuses and the solutions contained in them were weighed. From the weights of the solutions in the dilatometers and the measured volumes at the different temperatures, the volumes of weight-normal solutions at these temperatures were calculated by simple proportion in this way: Weight of solution : weight of the weight-normal solution :: volume found : volume required.

In making these calculations, a correction had to be introduced for the solution contained in the hole of the stop-cock. Its volume was determined by means of mercury, and was then added to the measured volume of the solution. The sum of the two volumes is the actual volume of the weight of solution contained in the apparatus for the given temperature. Having thus obtained the volume of the weighed amount of solution, its specific gravity was calculated. Knowing the volume of the hole in the stop-cock and the specific gravity of the solution, it was an easy matter to determine the weight of the solution contained in the opening of the stop-cock. This weight was then deducted from the total weight of the solution and the value thus obtained was the weight of solution whose volume had been measured at the temperature in question. This corrected weight was the one used for calculating the actual volumes of the weight-normal solutions.

For the calculations of the sum of the volumes of water and sugar contained in the various solutions, that is, for the determination of the volumes the solutions should have provided there was no contraction, the values 1.5813, as given by Gerlach and Kopp, and 1.5860 as given by Schroeder for the specific gravity of sugar in a vacuum at 15° were used, and the value .0001116 as given by Joule and Playfair for the coefficient of expansion of sugar.

The rotations given by the solutions before and after the experiments were as follows:

TABLE 1.

Weight—Normality of solutions.	Rotations	
	Before.	After.
0.1	12.60°	12.60
0.3	36.55°	36.55°
0.5	58.80°	58.70°
0.7	79.20°	77.50°
0.9	98.30°	75.00°

Tables 2 and 3 contain the results obtained at 15°. In Table 2, 1.5813 was taken as the specific gravity of sugar, and 1.5860 in table 3.

TABLE 2 (15°).

Weight—Normality of solutions.	Volume of water.	Volume of sugar.	Sum of vols. of water and sugar.	Measured volumes.	Difference in volumes in cc.
01.	1000.857	21.462	1022.319	1022.417	0.172
0.3	1000.857	64.386	1065.243	1063.952	1.291
0.5	1000.857	107.310	1108.167	1106.576	1.591
0.7	1000.857	150.234	1151.091	1147.462	3.629
0.9	1000.857	193.158	1194.015	1190.359	3.656

TABLE 3 (15°).

Weight—Normality of solutions.	Volume of water.	Volume of sugar.	Sum of vols. of water and sugar.	Measured volumes.	Difference in volumes in cc
0.1	1000.857	21.394	1022.251	1022.417	0.104
0.3	1000.857	64.182	1065.039	1063.952	1.087
0.5	1000.857	106.970	1107.827	1106.576	1.251
0.7	1000.857	149.758	1150.615	1147.462	3.153
0.9	1000.857	192.546	1193.403	1190.359	3.044

Tables 4 and 5 contain the results obtained at 20°. In Table 4, 1.5813 was taken as the specific gravity of sugar and 1.5860 in Table 5.

TABLE 4 (20°).

Weight—Normality of solutions.	Volume of water.	Volume of sugar.	Sum of vols. of water and sugar.	Measured volumes.	Difference in volumes in cc.
0.1	1001.751	21.474	1023.225	1023.111	0.114
0.3	1001.751	64.422	1066.173	1065.299	0.874
0.5	1001.751	107.370	1109.121	1107.870	1.251
0.7	1001.751	150.318	1152.069	1148.909	3.160
0.9	1001.751	193.266	1195.017	1191.827	3.190

TABLE 5 (20°).

Weight—Normality of solutions.	Volume of water.	Volume of sugar.	Sum of vols. of water and sugar.	Measured volumes.	Difference in volumes in cc.
0.1	1001.751	21.406	1023.157	1023.111	0.046
0.3	1001.751	64.218	1065.969	1065.299	0.670
0.5	1001.751	107.030	1108.781	1107.870	0.911
0.7	1001.751	149.842	1151.593	1148.909	2.684
0.9	1001.751	192.654	1194.405	1191.827	2.578

Tables 6 and 7 contain the results obtained at 25.° In Table 6, 1.5813 was taken as the specific gravity of sugar and 1.5860 in Table 7.

TABLE 6 (25°).

Weight—Normality of solutions.	Volume of water.	Volume of sugar.	Sum of vols. of water and sugar.	Measured volumes.	Difference in volumes in cc.
0.1	1002.911	21.486	1024.397	1024.343	0.054
0.3	1002.911	64.458	1067.369	1066.464	0.905
0.5	1002.911	107.430	1110.341	1109.404	0.937
0.7	1002.911	150.402	1153.313	1150.565	2.748
0.9	1002.911	193.374	1195.285	1193.707	3.578

TABLE 7 (25°).

Weight—Normality of solutions.	Volume of water.	Volume of sugar.	Sum of vols. of water and sugar.	Measured volumes.	Difference in volumes in cc.
0.1	1002.911	21.418	1024.329	1024.343(?)	+0.044(?)
0.3	1002.911	64.254	1067.165	1066.464	0.701
0.5	1002.911	107.090	1110.000	1109.404(?)	0.596(?)
0.7	1002.911	149.926	1152.837	1150.565	2.272
0.9	1002.911	192.762	1195.673	1193.707	1.966(?)

Instead of a contraction, an expansion appeared to have taken place in the case of the 0.1 weight-normal solution, which is probably due to some experimental error not yet detected, or possibly to the fact that an incorrect value for the specific gravity of sugar has been taken. The irregularity in contraction exhibited by the 0.5 weight-normal solution must be attributed to experimental error. In the case of the 0.9 weight-normal solution it may have been caused by decomposition of the solution which was indicated by the loss in rotation.

Tables 8 and 9 contain the results obtained at 30.° In Table 8, 1.5813 was taken as the specific gravity of sugar and 1.5860 in Table 9.

TABLE 8 (30°).

Weight—Normality of solutions.	Volume of water.	Volume of sugar.	Sum of vols. of water and sugar.	Measured volumes.	Difference in volumes in cc.
0.1	1004.314	21.497	1025.811	1025.777	0.034
0.3	1004.314	64.491	1068.805	1068.038	0.767
0.5	1004.314	107.485	1111.799	1111.106	0.693
0.7	1004.314	150.479	1154.793	1152.405	2.388
0.9	1004.314	193.473	1197.787	1195.631	2.156

TABLE 9 (30°).

Weight—Normality of solutions.	Volume of water.	Volume of sugar.	Sum of vols. of water and sugar.	Measured volumes.	Difference in volumes in cc.
0.1	1004.314	21.430	1025.744	1025.777	+0.033(?)
0.3	1004.314	64.290	1068.604	1068.038	0.566
0.5	1004.314	107.150	1111.464	1111.106	0.358(?)
0.7	1004.314	150.010	1154.324	1152.405	1.919
0.9	1004.314	192.870	1197.184	1195.631	1.553(?)

The same irregularities appear here as in Table 7. The 0.1 weight-normal solution seemed to have expanded instead of contracted. The 0.5 weight-normal solution showed a contraction, but it was not as large as might be expected. This is also true for the 0.9 weight-normal solution. The various irregularities here may be attributed to the same causes given under Table 7.

In Tables 10, 11 and 12 are given the expansion coefficients of the various solutions and of air-free water, as calculated from the experimental data.

TABLE 10.

Weight — Normality of solutions.	Volume at 15°.	Volume at 20°.	Difference	Expansion coefficients.
0.1	100.3734	100.4680	.0947	.000189
0.3	100.3952	100.5024	.1071	.000213
0.5	100.5779	100.6956	.1176	.000234
0.7	100.3743	100.5008	.1265	.000252
0.9	100.4533	100.5872	.1340	.000267
Air-free water.	100.4976	100.4976	.0880	.000175

The mean expansion coefficient of air-free water between 15° and 20°, as calculated from the values given in Landolt-Börnstein, is .000178.

TABLE 11.

Weight—Normality of solutions.	Volume at 20°.	Volume at 25°.	Difference	Expansion coefficients.
0.1	100.4680	100.5890	.1210	.000241
0.3	100.5024	100.6323	.1299	.000259
0.5	100.6956	100.8350	.1394	.000277
0.7	100.5008	100.6457	.1449	.000288
0.9	100.5872	100.7369	.1497	.000298
Air-free water.	100.6132	100.6132	.1156	.000230

The mean expansion coefficient of air-free water between 20° and 25°, as calculated from the values given in Landolt-Börnstein, is .000232.

TABLE 12.

Weight—Normality of solutions.	Volume at 25°.	Volume at 30°.	Difference	Expansion coefficients.
0.1	100.5890	100.7298	.1408	.000280
0.3	100.6323	100.7808	.1485	.000295
0.5	100.8350	100.9896	.1546	.000307
0.7	100.6457	100.8066	.1606	.000320
0.9	100.7369	100.8983	.1614	.000320
Air-free water	100.6132	100.7507	.1375	.000274

The mean expansion coefficient of air-free water between 25° and 30°, as calculated from the values given in Landolt-Börnstein, is .000280.

In Table 13 are given the expansion coefficients of the various solutions as calculated from the experimental data in terms of the volumes at 15°.

TABLE 13.

Weight—Normality of solutions.	Expansion coefficients 15°—20°.	Expansion coefficients 20°—25°.	Expansion coefficients 25—30°.
0.1	.000189	.000.241	.000280
0.3	.000213	.000259	.000296
0.5	.000234	.000277	.000307
0.7	.000252	.000288	.000320
.09	.000267	.000298	.000321

The solutions whose rotation changed during the investigation all contained a growth of some sort, probably penicillium. The results given in the tables for the concentrations greater than 0.6 normal are not reliable, because those were the solutions which contained more or less of the growth mentioned, and whose rotation had changed, in some cases very considerably.

It is possible to correct for inversion by taking the loss in rotation into account, but it would be useless to do so, since it can not be stated with certainty that further decomposition did not take place.

In spite of the numerous valueless results obtained, it seems evident from the foregoing results; (1) that, when cane sugar is dissolved in water at any given temperature, the contraction in volume increases with the concentration of the solutions; (2) that, for any given concentration, it decreases with rise in temperature.

BIOGRAPHY.

Henry Otto Eyssell was borin in Kansas City, Mo., February 23, 1885. He received his early education in the public schools of his native city. In September, 1904, he entered the Universar of Missouri, where he received the degree of Batchelor of Arts in June, 1908. In October, 1909, he entered the Johns Hopkins University as a graduate student in Chemistry.